N-Alkyl-*N*-methylpyrrolidinium salts as templates for hexagonally meso-ordered silicate thin films

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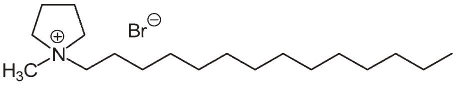
Received (in Cambridge, MA, USA) 29th September 2004, Accepted 24th November 2004
First published as an Advance Article on the web 24th December 2004
DOI: 10.1039/b415135f

A series of *N*-alkyl-*N*-methylpyrrolidinium bromide salts (C14, C16, or C18) have been explored as templates for the synthesis of ordered, mesoporous silica films; "soft" annealing based on deep-UV calcination is also reported.

Following the landmark report on the M41S family of silicate and aluminosilicate mesoporous molecular sieves by Kresge and colleagues at Mobil,[1] periodic mesoporous materials have aroused intense interest on account of their potential for elaborating tailored catalysts, adsorbents, membranes, low-*k* dielectrics, ion-exchange resins, and sensors.[2–6] These materials, typified by the MCM-41 (hexagonal *P6mm*) mesophase, are produced by a supermolecular templating mechanism using a variety of precursors in which diblock copolymers or surfactant assemblies serve as organic templates, for instance. There are several recent examples of the use of a new class of amphiphiles based on ionic liquids[7] to produce shape-selective, mesostructured inorganic materials. Invariably, these studies have employed long-chain 1-alkyl-3-methylimidazolium halides, hereafter designated C_nMIX (X = Cl^-, Br^-). For example, the Seddon group first reported MCM-41 prepared hydrothermally using C_nMIX salts as templates.[8] Later, Zhou and Antonietti used C_nMIX (n = 10, 14, 16, 18) templates to prepare mechanically stable monolithic silicas with ordered, lamellar super-micropores (12–15 Å pore diameters) using a nanocasting approach.[9] The same authors also used C_{16}MIX in concert with a polystyrene face centered cubic colloidal crystal as bimodal structure-directing co-templates to produce a super-microporous lamellar nanostructure imposed on an inverse opal microstructure.[10] Most recently, Dai and coworkers used C_{16}MIX to synthesize ethane-bridged silsesquioxane periodic mesoporous organosilicas (PMOs) under basic conditions.[11] No previous studies have appeared involving other promising classes of ionic liquid, such as the *N*,*N*-dialkylpyrrolidinium salts,[12–14] toward the preparation of such materials.

We report here on the synthesis of oriented, continuous mesoporous silica thin films prepared using *N*-alkyl-*N*-methylpyrrolidinium bromides, C_nMPB (Scheme 1), whose synthesis and surfactant properties were recently disclosed.[15] The films were formed *via* an evaporation-induced self-assembly (EISA)[4,16] procedure involving hierarchical organization of organic surfactant and inorganic silica building blocks. Tetraethyl orthosilicate (TEOS) was used as the inorganic precursor with C_nMPB, for n = 14, 16 or 18, as template.



Scheme 1 *N*-Tetradecyl-*N*-methylpyrrolidinium bromide, C_{14}MPB.

Film casting solutions were prepared by addition of C_nMPB to oligomeric silica sols made by a two-step sol–gel process[4] designed to minimize the siloxane condensation rate, promoting facile silica–surfactant co-assembly during film deposition.[17] In a typical synthesis, TEOS, ethanol, water (18.2 MΩ cm^{-1}) and HCl with initial mole ratios of 1 : 3.8 : 1 : 5 × 10^{-5} were refluxed for 90 min. After cooling to room temperature, a portion of the above was further diluted with ethanol and aqueous HCl (0.07 M) giving final reactant molar ratios of 1 TEOS : 22 EtOH : 5 H_2O : 0.004 HCl. Next, C_nMPB was added at a level well below the critical micelle concentration (cmc), typically 2.5–7.0 wt %, and the final mixture sonicated for 15 min. Thin films were deposited onto freshly oxidized, doubly polished, p-doped single crystal silicon wafers cut in the (100) direction by dip-coating at a withdrawal rate of 10.0 cm min^{-1} from the casting solution in an atmospherically-controlled chamber (25 °C, 40% relative humidity). After the films were aged for 2 d in covered Petri dishes, the templating surfactant microphase was removed from the resultant mesostructured nanocomposite thin films using either traditional thermal calcination or a deep-ultraviolet (DUV) photochemical treatment using a Hg lamp (184.9 and 253.7 nm lines). The latter, which involves *in-situ* photochemical production of the strong oxidants ozone and oxygen radicals,[18,19] has been shown to be an effective means for cleaning semiconductor surfaces[18] and for photolithographic micro-patterning of films.[16]

The resulting ordered silicate films were characterized by X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The low-angle XRD pattern for a typical as-prepared crack-free silicate film using C_{14}MPB as a template (nominally 200 nm thick as estimated by ellipsometry) is indicative of assembly of a one-dimensional hexagonal (1-dH) mesophase; d_{100} = 36.2 Å (Fig. 1A). A 1-dH topology was also observed for n = 16 and 18. The absence of the (110) and (210) mixed reflections observed in the XRD pattern of randomly-oriented hexagonal mesoporous silica powder indicates that the *c*-axis of the hexagonal unit cell (*i.e.*, the pore channel) is oriented parallel to the single crystal silicon surface.[1,2,4] The corresponding hexagonal unit cell constants, a_0, the distance between the centers of nearest pore neighbors, are collected in Table 1. As shown in Fig. 1B, linear extrapolation to $n = 0$ in a plot of a_0 for the as-prepared films *versus* the alkyl chain length (n) of the structure-directing agent allows the thickness of the siloxane interpore layer to be estimated. The resulting value, 6.4 ± 0.5 Å, is a factor of 2 or 3 lower than that typically seen.[3] As anticipated, thermal calcination (Fig. 1A, trace c) results in a shift of the (100) reflection,

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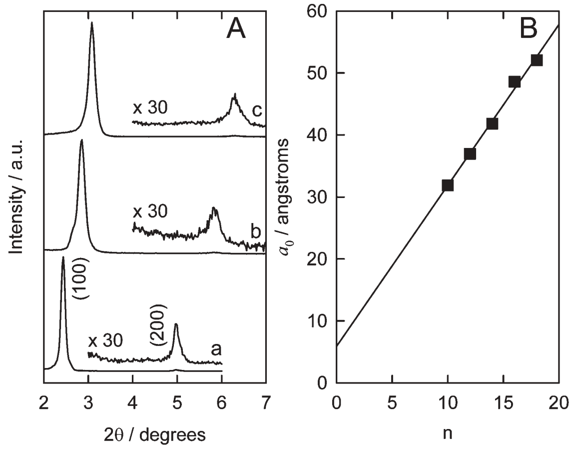

Fig. 1 (A) XRD patterns for oriented silica thin films grown on (100)-silicon using C_{14}MPB as a template. Trace a, as-synthesized; trace b, photocalcined; trace c, calcined in air at 450 °C for 4 h. XRD data were collected on a Scintag XDS 2000 using CuKα radiation, $\lambda = 1.5418$ Å. (B) Variation in a_0 values as a function of the C_nMPB acyl-chain length.

Table 1 Unit cell constants, a_0/Å, for supported hexagonal films prepared by EISA using C_nMPB templates[a]

n	As-prepared	DUV[b]	Thermal[c]
14	41.8	35.7	33.1
16	48.6	—	37.8
18	52.0	47.7	42.9

[a] The hexagonal unit cell parameter $a_0 = 2\ d_{100}/\sqrt{3}$. [b] Photocalcination of the mesostructured thin films was accomplished *via* a 90–120 min exposure from a medium-pressure Hg grid lamp (10–20 mW cm^{-2}, UVP, Inc.) placed *ca.* 2 cm above the substrate. [c] Following a 2 °C min^{-1} temperature ramp, samples were calcined in air at 450 °C for 4 h.

corresponding to a 21% decrease in the a_0 from 41.8 to 33.1 Å. Interestingly, on photocalcination of a virgin film, a somewhat smaller contraction (< 15%) is observed for the TEOS/C_{14}MPB film. For C_{18}MPB as the organic template, a significant reduction in contraction is observed in going from thermal to photochemical calcination, with corresponding decreases in a_0 of 17.6 and 8.4%, respectively. Typical values for the degree of contraction taken from the literature are in the 15–25% range suggesting that DUV treatment is a softer alternative to conventional calcination in the preparation of mesoporous materials.[1–6] Shorter-chain templates ($n = 10, 12$) presumably gave lamellar structures as elimination of the organic phase led to systematic pore collapse and complete loss of mesostructure.

Efficient and selective template removal by DUV exposure was confirmed by IR studies. Interestingly, the peak frequencies of the $\nu(CH_2)_s$ and $\nu(CH_2)_{as}$ stretching modes in the as-prepared films (2854 and 2925 cm^{-1}, respectively), structural probes of the chain conformation,[20] suggest some gauche character of the aggregated aliphatic chains in the hexagonal micellar mesophase. It is also noteworthy that the single CH_2 scissoring mode at 1467 cm^{-1} has been attributed to hexagonal subcell packing earlier.[21] As shown in Fig. 2, disappearance of these template-specific signatures indicates a complete loss of the C_{14}MPB microphase following either calcination mode. In contrast, the intense antisymmetric Si–O–Si stretching modes in the 950–1250 cm^{-1} window showed no significant changes as a result of photo- or thermal calcination. Consistent with the XRD results, the lack of broadening for the antisymmetric Si–O–Si bands upon photocalcination (Fig. 2A, trace b) suggests that the silicate skeleton is perfectly preserved upon surfactant removal. While the strongly coupled antisymmetric (ν_3) and symmetric (ν_1) water stretches in the 3300–3500 cm^{-1} region are lost upon thermal treatment at 450 °C, coupled with the emergence of the sharp peak at 3746 cm^{-1} assigned to the free (isolated, non-hydrogen bonded) Si–OH stretch and the loss of the H-bonded Si–OH feature at 945 cm^{-1}, the films are only partially dehydrated after DUV exposure. Ellipsometrically-determined indices of refraction measured 24 h after surfactant removal for using thermal and DUV treatments (*ca.* 1.3 and 1.4, respectively) are fully consistent with this view. Further to this, the shift to higher wavenumber for the broad envelope centered at about 3300 cm^{-1} reflects a reorganization of the water within the DUV exposed mesoporous films and is consistent with evolution of water as a result of light-promoted condensation between adjacent vicinal and geminal silanols resulting in an increase in the relative number of Q4 sites.[16,19]

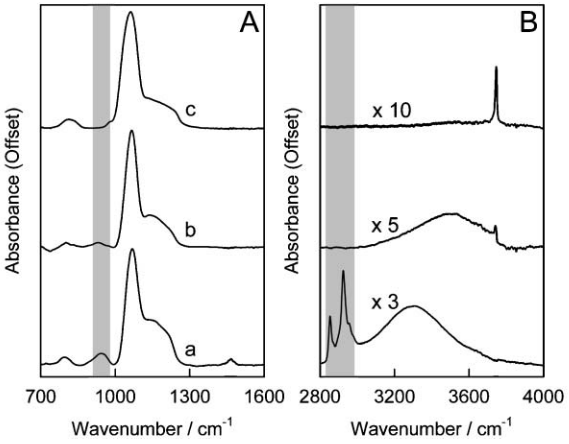

Fig. 2 Transmission FT-IR spectra for C_{14}MPB-templated ordered silicate thin films. Sample descriptions for traces a, b, and c are the same as for Fig. 1. Spectral regions discussed in the text are highlighted. All reported spectra were obtained by co-adding 256 scans collected at 4 cm^{-1} resolution using a Bruker Equinox55.

In summary, C_nMPB ionic liquid analogs have been shown as effective mesostructuring agents in the preparation of uniform oriented mesoporous thin films formed *via* an EISA approach. DUV exposure was also found to be a nonthermal alternative for removal of the organic microphase leading to a strengthened mineral network with minimal contraction of the hexagonal pore lattice. Given the technological relevance of the thin film motif, we can anticipate a range of potential applications for these materials in membrane filtration, sensor arrays, optics, microelectronics, medical applications and catalysis.

This work was supported by the U.S. Department of Energy Office of Basic Energy Sciences. GAB acknowledges a Frederick Reines Fellowship which allowed him to undertake this work.

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